



## Chlorination and characterization of natural rubber and its adhesion to nitrile rubber

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### ABSTRACT

Chlorinated natural rubber (CNR) vulcanized sheets were prepared by immersing the NR sheets in sodium hypochlorite solution for various chlorination times ranging from 0 to 30 min. The degree of chlorination as indicated by X-ray Absorption Near-Edge Spectroscopy (XANES) implied that the chlorine content increases with the chlorination time from 0 to 10 min then levels off. Atomic Force Microscopy (AFM) showed an evolution of the surface roughness and stiffness. These two properties increased gradually with chlorination time. The bond strength between CNR and nitrile rubber (NBR) also increased gradually. The data showed cohesive failure beginning at 1 min and extending throughout the 30 min of the study. The maximum peel strength was found at 1 min of chlorination time and decreased afterwards. The decrease in peel strength was caused by the increase in surface stiffness of NR that acted as weak boundary layer. The surface stiffness governed the peel strength between NR and NBR.

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### 1. Introduction

Chlorination of natural rubber (NR) surface is often carried out to reduce the tackiness and frictional resistance, especially in surgical and household NR groves [1]. Several studies have reported on the improvement of the adhesion of rubbers with other materials by using surface chlorination [2–7]. In footwear industry, styrene butadiene rubber (SBR) is chlorinated to improve the bonding with polyurethane adhesive. Treatment method could be achieved via several techniques e.g. plasma chlorination, acidified hypochlorite solution, chloramine solution as well as trichloroisocyanuric acid solution. However, undesirable reactions for example cyclization and chain scission may also occur

[8]. Chlorination of rubber also produces chemical and physical changes on modified surface. Chemical linkages could be created between substituting chlorine and proper functional groups e.g. carboxylic acid or ester [9]. A physical change on chlorinated rubber surface has also been reported. Ho and Khew [10] found microcracks structure on chlorinated surface of unvulcanized NR. This structure contributes to the adhesion strength because of the increase in contact surface area. The high degree of chlorination leads the treated surface becoming too stiff. This acts as limiter of adhesion strength. The chlorination of rubber surface produces both chemical and physical changes. The changes have to be balanced to achieve optimum properties. The aim of this investigation is to improve poor properties of NR (e.g. heat and oil resistance) by encasement with nitrile rubber (NBR). Bond strength between NR and NBR could determine the life span of such product. This work reports and discusses the effects of chlorination on the chemical and physical changes of vulcanized NR surface that affected the adhesion property between NR and NBR.

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## 2. Experimental

### 2.1. Materials

NR used was Standard Thai Rubber (STR5L) purchased from Rayong Rubber Co. Ltd. Zinc oxide (ZnO) and stearic acid were used as the curing activator and were supplied by Petch Thai Co. Ltd. and Polychem Co. Ltd., Thailand, respectively. Tetramethyl thiuramdisulfide (TMTD), *N*-tert-butyl-2-benzothiazole sulfenamide (TBBS) from Flexsys (Thailand), and sulfur from Siam Chemicals Co. Ltd., respectively, were employed as curatives. Carbon black N330 from Thai carbon black Co. Ltd. was used to reinforce the rubber vulcanizate. Sodium hypochlorite (NaOCl) with 6–14% available chlorine content and NH<sub>4</sub>OH solution (25%) were purchased from Merck and hydrochloric acid (37%) was provided from Fluka. Chloranil (tetrachloro-*p*-benzophenone) was supplied by Fluka and was used as standard for calibration of chlorine density on NR surface.

### 2.2. Preparation of rubber compounds

NR or NBR and other ingredients were separately mixed by using an internal mixer. Rubber was first charged to reduce its viscosity (mastication) before adding carbon black N330. The mixtures were continuously mixed until a constant viscosity was attained. The activator was then added following by curatives in the last step. NR compound was sheeted and cured to form sheet by hydraulic hot pressing at 155 °C for period depending on the cure time ( $T_{90}$ ) obtained from a curometer. The NBR compounds were pressed to form sheet of 2 mm thickness at 80 °C. They were then pressed together with CNR sheet for cure time of NBR compound at 155 °C. The formulation of the rubber compounds are presented in Table 1.

### 2.3. Chlorination

Chlorination solution was a mixture of NaOCl:HCl:H<sub>2</sub>O at 2:1:100 by volume. The solution was freshly prepared before their used for each chlorination treatment in order to limit loss of chlorine available content during treatment. The whole surface of the cured NR sheet was cleaned with acetone prior to immersion in chlorination solution for various times. The specimen was neutralized in 2% NH<sub>4</sub>OH and deionized water, respectively. They were then dried in vacuum oven at 40 °C for 24 h.

**Table 1**  
Formulation of NR and NBR compounds.

	Content (phr <sup>a</sup> )	
	NR	NBR
Rubber	100	100
N330	40	40
ZnO	3	3
Stearic acid	1	1
Sulfur	1.5	0.5
TMTD	–	1.5
TBBS	1.5	–

<sup>a</sup>Part per hundred of rubber.

### 2.4. Infrared spectroscopy

The CNR surfaced were characterized using a BRUKER, model Equinox 55 Fourier Transform Infrared Spectroscopy. The treated sample surfaces were pressed against the Ge crystal to obtain the spectra which were recorded during 64 scans at a resolution of 4 cm<sup>-1</sup>. The penetration depths under the treated surface were approximately 5–10 μm.

### 2.5. Atomic Force Microscopy

An Atomic Force Microscope – Multimode Nanoscope IIIA from Digital Instruments, Santa Barbara, USA, was employed to investigate the topology, surface roughness, adhesion force and stiffness in contact mode. The specimen was probed with silicon nitride (Si<sub>3</sub>N<sub>4</sub>) tip at spring constant of 0.12 N/m. Tip velocity of 5 μm/s was used. The height and deflection images were recorded with the resolution of 512 lines. The arithmetic mean roughness ( $R_a$ ) was analyzed on height image before flattening with the second order plane fit that was implied to remove the tilt and distortion in the images.  $R_a$  was derived from

$$R_a = \frac{\sum_{i=1}^N |Z_i - Z_{ep}|}{N} \quad (1)$$

where  $Z_i$  and  $Z_{ep}$  were current and center plane of  $Z$  value, respectively,  $N$  was number of determined points within given area.

Relative surface stiffness and adhesion force between tip and surface of chlorinated rubber at various immersion times was determined by using Force Distance Curve (FDC) at 5 Hz. Silicone wafer was used as hard surface to compare the stiffness on the slope of extending line with rubber samples, whereas adhesion force ( $F_{adh}$ ) was determined on hysteresis loop of retracting line, calculated as following:

$$F_{adh} = k \Delta z \quad (2)$$

$k$  was spring constant of cantilever (0.12 N/m) and  $\Delta z$  was distance on  $Z$  scale.

### 2.6. X-ray Absorption Near-Edge Spectroscopy (XANES)

Chlorinated NR film was separately prepared into 100–200 μm thickness accurately. It was determined the density of chlorine substitution onto NR surface quantitatively. The range of photon energy at 2810–2880 eV with beam dimension of 10 × 1 mm<sup>2</sup> were used. The data was analyzed using MATLAB program in order to translate them to edge jump which corresponded to energy absorption intensity. The density of chlorine atom on the surface was calculated comparing with a standard calibration curve of chloranil (C<sub>6</sub>O<sub>2</sub>Cl<sub>4</sub>) diluted with activated carbon.

### 2.7. Peel strength

Specimen for peel test was prepared by pressing together the NBR sheet with CNR. Pressing condition was controlled according to  $T_{90}$  of NBR compound at 155 °C. Bond strength

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